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WO 02/12119

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PCT/FR01/02527

PROCESS FOR THE PREPARATION OF PHOSPHORUS PENTOXIDE  
POWDER HAVING IMPROVED FLOWABILITY

The present invention relates to a process  
5 for the preparation of phosphorus pentoxide (hexagonal  
variety), hereinafter  $P_2O_5$ , powder having improved  
flowability.

$P_2O_5$  is obtained industrially by combustion of  
white phosphorus in a stream of dry air in large  
10 excess. The reaction is exothermic and causes the  
temperature to rise to approximately 1 300°C. The  
combustion gases which result therefrom, consisting of  
a mixture of air depletes in  $O_2$  and of gaseous  $P_2O_5$ , are  
conveyed to a condenser (desublimator), where  $P_2O_5$   
15 crystallizes in the powder form. Subsequently, the  $P_2O_5$   
powder obtained is generally sieved and then packaged  
in kegs or in containers.

$P_2O_5$  is an important industrial product. It is  
used in particular as intermediate reactant in the  
20 preparation of numerous phosphoric esters, used in  
particular in the agrochemical or pharmaceutical  
fields. These phosphoric esters are generally obtained  
by reacting solid  $P_2O_5$  with an alcohol (generally in the  
liquid form or in solution). These reactions employ two  
25 different stages and require the presence of an  
efficient mixing method and a suitable means for  
introducing the  $P_2O_5$  powder, in order to adhere to the

stoichiometry and the kinetics of the reactions and to avoid excessively abrupt evolutions of heat when the  $P_2O_5$  powder is introduced.

It is therefore necessary to have a  $P_2O_5$  powder which has good processing properties, good transportation properties and good properties of dispersion in a reaction medium, in particular good flowability (or flow).

The term "flowability" denotes here the ability which a powder possesses to flow in a stable, uniform and even fashion in the form of individual particles through a narrow or wider orifice.

Numerous tests make it possible to determine the flowability of powders.

The "tamping" test is generally regarded as being the most appropriate for the evaluation of the flowability of  $P_2O_5$  powders.

This test consists in measuring the ability of a powder to tamp down under the action of small impacts produced by a standardized rod. The measurement consists in estimating the difference between the initial volume and the volume occupied after 500 blows. The more a powder tamps down, the poorer its flowability.

On the basis of this test, three indices can be determined:

- the aerated apparent density  $d_a$ ,

- the tamped apparent density  $d_t$ , and
- the Hausner ratio  $H_r$ , which is equal to the  $d_t/d_a$  ratio.

When  $H_r$  decreases, the flowability of the  
5 powder improves as the density  $d_a$  approaches the density  $d_t$ .

In other words, the spaces between particles are more difficult to fill in with other smaller particles. The accumulation of these fines between the  
10 particles of various size leads to an increase in the interparticular forces, thus impeding the overall flow of the powder. The  $H_r$  ratio is therefore revealing of the arrangement of the particles with regard to one another. Thus, a  $P_2O_5$  powder exhibiting an  $H_r$  ranging  
15 from 1 to 1.25 exhibits few processing problems. The density  $d_a$  is close to the density  $d_t$ .

The tamped apparent density  $d_t$  alone is certainly not an index of flowability; however, its determination complements the knowledge of  $H_r$  insofar  
20 as, for a powder with a given particle size, if the density  $d_t$  is high, then the gravitational forces become greater than the interparticular forces, resulting in natural flow being promoted. For the same  $H_r$ , when  $d_t$  decreases, flow is promoted.  $H_r$  is a nondimensional  
25 parameter;  $d_t$  makes it possible to compare powders with one another.

The aerated (or true) apparent density  $d_a$

cannot be used either as index of flowability but is used in techniques for the transportation and packaging of  $P_2O_5$  powders.

The Applicant Company has found that, in the industrial preparation of  $P_2O_5$  as mentioned above, it obtained, in an entirely random fashion, batches of  $P_2O_5$  powder having poor flowability (high Hr) prohibiting it from being subsequently used, in particular from being used as intermediate reactant for the synthesis of phosphoric esters.

Patent EP 189 766 B1 discloses a process which makes it possible in particular to improve the flowability of  $P_2O_5$  powders. This process consists in heating  $P_2O_5$  (hexagonal variety) powders at temperatures ranging from  $200^\circ C$  to  $390^\circ C$  for 0.5 to 8 hours in a closed and optionally stirred reactor.

This process makes it possible to obtain a substantial improvement in the flowability of  $P_2O_5$  powders, an improvement obtained, however, by using high temperatures and lengthy "annealing" times, which conditions put a considerable strain on the productive capacity of an industrial process. In addition, this process requires an expensive investment in equipment.

In addition, this heat or annealing treatment lowers the "reactivity" of the  $P_2O_5$  (hexagonal variety) powder. This reactivity is evaluated by a simple test which consists in reacting a solution of  $P_2O_5$  in an

aromatic solvent, such as ortho-dichlorobenzene, with a phenol.

The measurement is then made of the evolution of heat produced by the reaction over a predetermined  
5 period of time.

The reactivity of the  $P_2O_5$  is therefore quantified in  $^{\circ}C/min$ .

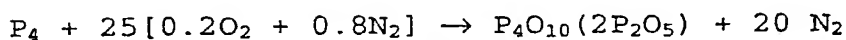
This reactivity, specific to hexagonal  $P_2O_5$ , is a characteristic increasingly required by many users  
10 of  $P_2O_5$ , who wish to have a  $P_2O_5$  powder having good flowability and high reactivity.

The Applicant Company has found that it is possible to obtain a  $P_2O_5$  (hexagonal variety) powder which has improved flowability, which has good  
15 dispersion and which retains high reactivity, by subjecting the  $P_2O_5$  powder to a mechanical treatment by the dry route at ambient temperature.

The subject-matter of the invention is therefore a process for the preparation of a phosphorus  
20 pentoxide (hexagonal variety) powder with improved flowability, characterized in that said powder is subjected to mechanical stirring by the dry route at ambient temperature under a dry gas atmosphere for a period of time ranging from 5 minutes to 30 minutes and  
25 preferably of between 10 and 20 minutes.

The  $P_2O_5$  powder subjected to such a mechanical treatment can have various origins.

It can originate from a  $P_2O_5$  powder storage area. It can also originate directly from a process for the manufacture of  $P_2O_5$ , which consists in continuously introducing liquid white phosphorus and dry air in excess, with respect to the stoichiometry of the reaction:



into a combustion region, in cooling the combustion gases exiting from this region of the in condenser (or desublimators), in recovering the  $P_2O_5$  powder obtained in said condensers and in conveying it by means of a screw conveyor to a mechanical treatment region according to the present invention.

In this case, the  $P_2O_5$  powder obtained, exiting from the screw conveyor, can be at a temperature slightly greater than ambient temperature.

According to the present invention, the term "ambient temperature" denotes a temperature ranging from  $15^\circ C$  to  $30^\circ C$  and preferably of between 20 and  $25^\circ C$ . This temperature is the temperature of the mechanical treatment and means that said treatment is carried out in a device which is neither heated nor cooled.

According to the present invention, the mechanical treatment of the  $P_2O_5$  powder is carried out by the dry route. This means that no solvent is used during this treatment.

The treatment is carried out under an atmosphere of a dry gas, such as air. The use of an inert gas is not necessary.

According to the present invention, the  
5 mechanical stirring operation can be carried out in any device allowing efficient deagglomeration of powders.

Use will preferably be made of "plowshare" mixers which exhibit a stirring rate ranging from 100 rev/min to 350 rev/min and preferably ranging from  
10 150 rev/min to 300 rev/min and which make it possible to obtain a Froude number  $Fr$ , representing the ratio of the centrifugal forces to the gravitational forces, which can range up to 5.

The charge of the powder subjected to  
15 stirring in the mixer is defined by the power per mass  $P_m$ , according to the relationship:

$$P_m = \text{kW/kg of product to be treated (kW.kg}^{-1}\text{)}$$

The stirring time is short; generally 10 to 15 minutes is sufficient to produce a powder of good  
20 flowability, that is to say a powder exhibiting an  $H_r \leq 1.25$ .

According to the present invention, the stirred  $P_2O_5$  powder is transferred to a storage area before it is packaged.

25 The process according to the present invention exhibits the advantage of resulting in a  $P_2O_5$  powder which has good processing properties, in

particular good dispersion, and good flowability  
( $Hr \leq 1.25$ ), this being achieved without addition of  
any anticaking agent, and which also exhibits a  
reactivity at least equal to, indeed even greater than,  
5 that measured before the mechanical treatment.

The following examples illustrate the  
invention.

EXAMPLES:

Production of the  $P_2O_5$  powder:

10 The  $P_2O_5$  powder was obtained in a plant as  
represented diagrammatically in figure 1, according to  
a process which consists in continuously introducing  
liquid white phosphorus via the pipe (1) and dry air  
via the pipe (2) into a combustion region (3) composed  
15 of a cooled cylindrical chamber.

The combustion gases exiting from the  
combustion region at a temperature of between  $600^\circ\text{C}$  and  
 $650^\circ\text{C}$  are conveyed via the pipe (4) to a cylindrically-  
shaped condenser (5) terminated by a frustoconical  
20 part, cooled by a film of water with a regulated flow  
rate, in which the solid  $P_2O_5$  particles are formed in  
the cooled gases and grow until precipitating within  
the gas mixture to form a finely divided solid mass  
which falls to the bottom of said condenser into the  
25 hopper and which is subsequently conveyed by means of a  
screw conveyor belt (6) and a pipe (7) to a mixer (8)  
where it will be subjected to the mechanical treatment



according to the invention.

The gases exiting from the condenser (5) are conveyed via the pipe (9) to a second condenser (10), identical to the condenser (5), from which  $P_2O_5$  powder is also recovered, the powder falling into the same screw conveyor (6).

The gases exiting from the condenser (10), composed of depleted air, are discharged into the atmosphere via the pipe (14).

10 The treated powder is conveyed via the pipe (11) to a storage area (2) from which packaging is carried out via (13).

$P_2O_5$  powder is withdrawn before and after the mixer (8), via a device not represented in figure 1, in order to determine its flowability and reactivity characteristics.

The operating conditions for the manufacture of the  $P_2O_5$  powders are listed below in table 1.

Conditions	Flow rates	
	Liquid white phosphorus (kg/h)	Dry air ( $Sm^3/h$ )
A	180	1 100
B	100	700

Mechanical treatment of the  $P_2O_5$  powders obtained according to conditions A and B:

Device used:

Plowshare mixer of MXC 0150 type with a capacity of 150 liters, sold by Gericke

Mechanical treatment conditions:

- temperature: approximately  $25^{\circ}C$
- stirring rate (rev/min): 300
- charge (kg): 80
- 10 - power per mass  $P_m$  ( $W.kg^{-1}$ ): 56
- stirring time (min): 15
- gas used: dry air.

Results of the treatment:

The characteristics:

- 15 - aerated density  $d_a$ ,
- tamped density  $d_t$ ,
- Hausner ratio  $H_r = d_t/d_a$ , and the reactivity of the  $P_2O_5$  powders treated according to the invention and of the untreated  $P_2O_5$  powders are listed in table 2.
- 20 These characteristics were determined by using the tests below.

Tamping test:

Principle:

- 25 The  $H_r$  ratio measures the ability of the particles to tamp down under the action of small standardized impacts. A predetermined amount of powder

is poured into a measuring cylinder. The measurement then consists in recording the initial volume of the sample and then the volume occupied by the powder after a chosen number of impacts.

5                   The Hr ratio is determined with a volumeter.

Equipment:

- glove box under dry air,
- volumeter (device used to tamp down the powder in accordance with Standards ISO R787 and ASTM B522 70),
- 10 - 250 ml round-based measuring cylinders,
- balance,
- stainless steel funnel,
- stainless steel sieve with a diameter of 2 mm,
- stainless steel scoop,
- 15 - spatula,

which are washed and dried in an oven at 80°C.

Procedure:

1. The powder to be analyzed is sieved, so as to remove the various cases of tamping due to prior handling operations.
- 20       2. 100 g, plus or minus 2 g, are placed in a measuring cylinder using the funnel. To allow the powder to flow, a stainless steel plate is regularly tapped against the funnel, care being taken not to touch the
- 25       edge of the measuring cylinder. Care also has to be taken not to tamp down the powder and not to deposit too much of it along the glass of the measuring

cylinder. The mass and the volume are recorded.

3. The measuring cylinder is placed on the volumeter and 500 blows are applied by it. This operation is repeated three times.

5 Calculation:

Aerated density: Mass of powder introduced into the measuring cylinder/initial volume (before tamping)

Tamped density: Mass of powder introduced into the measuring cylinder/final volume (after tamping)

- 10 Hausner ratio: Hr: Tamped density/Aerated density

Interpretation of the results:

Hr  $\leq$  1.25: very good ability to flow,

1.26  $\leq$  Hr  $\leq$  1.30: good ability to flow,

1.31  $\leq$  Hr  $\leq$  1.4: flow difficult,

- 15 Hr  $>$  1.4: free flow virtually impossible.

Reactivity test:

Principle:

- 20  $P_2O_5$  is reacted with a phenol. The change in temperature of the mixture as a function of time is recorded and the reactivity is determined by the measurement of the slope of the tangent to the point of inflection of the curve: temperature = f(time).  
Temperature of the beginning of the test: 25°C

- 25 Introduction of the phenol all at once.

Reactants:

- xylenol (2,4-dimethylphenol)

- ortho-dichlorobenzene

Equipment:

- 1 direct-current stirrer with a speed counter which is equipped with an anchor stirrer,
- 5 - 1 temperature-recording device equipped with an iron/constantin thermocouple probe,
- 1 bath adjustable to 25°C,
- 1 laboratory balance,
- 1 Dewar flask.

10 Procedure:

- the bottles of reactants are placed in the heating bath, adjusted to 30°C,
- ~~the Dewar flask is washed with hot water and is dried~~  
with acetone,
- 15 - 20 g of  $P_2O_5$  are weighed out exactly in the clean and dry Dewar flask,
- the Dewar flask is placed on a rubber ring and the stirrer is adjusted so as to leave the least possible space between the stirrer and the wall of the flask
- 20 (approximately 1 mm),
- it is confirmed that the anchor of the stirrer rotates freely without rubbing against the walls of the flask,
- 44 cm<sup>3</sup> of ortho-dichlorobenzene are measured out
- 25 using a measuring cylinder,
- the ortho-dichlorobenzene is poured into the flask while rinsing the walls thereof,

- the stirring rate is adjusted to 300 rev/min,
  - 56.5 g of xyleneol are weighed out in a beaker,
  - the thermocouple is adjusted (the temperature must be 25°C),
- 5 - the xyleneol is poured into the flask and the recorder, calibrated beforehand, is started: rate of progression of the paper 6 cm/min,
- the recording is halted as soon as the temperature reaches 80°C.

#### 10 Results:

The tangent to the point of inflection of the curve of temperature as a function of time is plotted.

Its slope determines the reactivity of the  $P_2O_5$  powder in °C/min.

Test	Conditions for the manufacture of the $P_2O_5$ powder	Mechanical treatment according to the invention	Characteristics of the powder			
			Density (kg/m <sup>3</sup> )		Hr. ( $d_t/d_a$ )	Reactivity (°C/min)
			Aerated ( $d_a$ )	Tamped ( $d_t$ )		
1	A	no	866	1 118	1.29	4
	A	yes	1 041	1 272	1.22	8.5
2	B	no	629	851	1.35	6
	B	yes	877	1 087	1.24	12.5

TABLE 2